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Impurity Effects on Heterogeneous Nucleation from the Vapor: Selenium on Glass

By

Bernhardt E. Kreissner

and

John B. Hudson

Department of Materials Engineering

Rensselaer Polytechnic Institute

Troy, New York

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ABSTRACT

It has long been recognized that impurities adsorbed on the substrate can have a marked influence on the kinetics of heterogeneous nucleation. However, the detailed nature of these effects has not been demonstrated heretofore. In the present work, impurity effects have been characterized for the nucleation of selenium vapor onto Pyrex glass. It is shown that the degree of surface contamination not only affects the critical supersaturation required for nucleation, but may cause a nucleated phase of other than equilibrium structure. It is also shown that the degree of material accommodation for selenium on Pyrex is affected by surface contamination. These results are discussed in terms of the changes in substrate and nucleus interfacial energies accompanying impurity adsorption, and in terms of the possible masking of ordering influences exerted by a clean substrate.

INTRODUCTION

Results of recent studies of the kinetics of heterogeneous nucleation from the vapor[1,2] have shown significant departures from the predictions of classical nucleation theory. In general, the observed temperature dependence of the critical supersaturation ratio, which is the parameter most often measured in such work, has been shown to be much larger than that predicted by theory. An attempt was made, in this previous work, to explain the observed results in terms of poor thermal accommodation of the nucleant vapor at the substrate surface. More recently, measurements by Ruth, Moazed, & Hirth[3] of zinc nucleation on glass, in which thermal accommodation effects were explicitly sought after, indicated that such effects were indeed present, but were much too small to explain the temperature dependence of the previous measurements. The present work was thus undertaken both

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1. Hudson, J.B., Journal of Chemical Physics, vol. 36, no. 4 pages 887-889 (1962)1
2. Rutner, E., Goldfinger, P., Hirth, J.P., Eds., Condensation and Evaporation of Solids, Gordon and Breach, New York pages 639-648, (1964)
3. Ruth, V., Moazed, K.L., Hirth, J.P., "The Effect of Beam Temperature on the Heterogeneous Nucleation of Zinc from the Vapor", Ohio State University

to check for the presence of thermal accommodation effects in yet another system, and, in addition, to observe the effect of varying impurity levels on the kinetics of the nucleation process. It developed during the course of the work that the impurity associated effects were of much greater significance. Consequently, the characterization of these effects occupies the bulk of this paper.

THEORY

In order to develop a feeling for the possible effects of impurities on the nucleation process, let us consider, schematically, the steps in the formation of a nucleus. Referring to Figure 1, we see that the initial step in the process is the formation of an equilibrium adsorbed layer (adlayer) of coverage n_1, (moles/cm^2), where n_1 is given by $n_1 = n_o \exp\left[\frac{\Delta G_{des}}{RT}\right]$ where n_o is the density of adsorption sites on the surface and ΔG_{des} the Gibbs free energy of desorption. Once an equilibrium adlayer is formed, clusters of the nucleant species build up within the layer by a series of bimolecular reactions, the rate of which is limited primarily by surface diffusion. The Gibbs free energy of formation of these clusters, at small sizes, is positive. However, a finite population will exist at equilibrium through statistical fluctuations. In

time, certain of these clusters reach a critical size such that further growth results in a reduction of the free energy of the system; they can then grow to macroscopic size without further limitation. The critical size, i^*, is that at which the cluster free energy of formation, ΔG_i, goes through a maximum with increasing cluster size. The coordinates of this maximum are given by (for a spherical cap-shaped nucleus):

$$\Delta G_i^* = \frac{16\,\pi\,\sigma^2_{n-v}\,\phi_1(\theta)}{3\,\frac{kT^2}{\Omega}\,\ln^2\alpha}$$

$$i^* = \frac{32\,\pi\,\sigma^3_{n-v}\,\phi_2(\theta)}{3\,\frac{k^2T^2}{\Omega^2}\,\ln^2\alpha}$$

where σ_{n-v} is the nucleus-vapor interfacial energy, $\phi_1(\theta)$ and $\phi_2(\theta)$ are geometric functions of the substrate-nucleus contact angle, θ, Ω is the volume per molecule, and α, the supersaturation ratio, is defined by

$$\alpha = P/Pe$$

where P is the actual pressure of the condensing species in the system, and Pe is the equilibrium vapor pressure of the condensing species at the existing substrate temperature. The net rate of cluster formation, that is, the nucleation rate, is given by

$$J = c_1 n_1 \exp\left(\frac{\Delta G_{des} - \Delta G^*_{SD} - \Delta G_i^*}{kT}\right)$$

where c_1 is a frequency factor of order 10^{17} and ΔG^*_{SD}

is the activation free energy for surface diffusion.[4]

Consider now the points at which this sequential process can be affected by impurity adsorption, either on the substrate itself or on the forming clusters. There is first the possible effect of previously adsorbed impurities on the adsorption of the nucleant species -- this may show itself either in a weakening of the binding between substrate and adsorbate, or by affecting the energy transfer process between substrate and vapor and thereby changing the degree of thermal accommodation. Either of these effects will most likely operate to reduce the equilibrium adsorbed concentration n_1 and consequently the nucleation rate. There is also the possible effect of adsorbed impurities on the surface diffusion rate in the adlayer which could tend to reduce the rate of cluster formation and consequently the nucleation rate. Finally there is the effect of impurity adsorption on the surface and interfacial energy terms which enter the equation for ΔG_1^*. These terms will also act to increase ΔG_1^* and consequently to reduce the nucleation rate. It is possible that this last effect could, in addition, affect the morphology of the nucleus by

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4. Preceding theory adapted from: Chalmers, Bruce, Ed., Progress in Materials Science, Vol. XI, Hirth, J.P., and Pound, G.M., "Condensation and Evaporation", Pergamon Press, Oxford, (1963)

changing the relative surface energies for different morphologies or orientations to the point where the nucleus of lowest ΔG_i^* had a different form than in the case of nucleation on a clean surface.

In the present work, the nucleation behavior was characterized by using the well-known technique of measuring the critical supersaturation required for observable nucleation.[5] The expected rate equation for this technique has been shown by classical nucleation theory to be

$$\ln \alpha_{crit} = \frac{16 \pi \Omega^2 \sigma_{n-v}^3 \phi_i(\theta)}{3 k^3 \ln \left[\frac{(const) n_1}{J_{crit}} \right]} \frac{1}{T_s^{3/2}}$$

in which J_{crit}, the smallest observable nucleation rate, is usually taken to be about one/cm^2-sec for measurements made by the visual observation technique employed in the present work, and T_s is the temperature of the adlayer. From the foregoing discussion it is apparent that one would expect impurity adsorption to increase the absolute value of α_{crit}, but not the dependence of α_{crit} on temperature, unless there are thermal accommodation effects which change T_s from the measured substrate temperature.

EXPERIMENTAL

Critical supersaturation measurements were made for selenium

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5. Chalmers, Bruce, Ed., Progress in Materials Science, Vol. XI, Hirth, J.P., and Pound, G.M., "Condensation and Evaporation," Pergamon Press, Oxford (1963)

on Pyrex in two different experimental configurations. In the first, the surface was exposed to a free vapor of selenium inside a sealed, evacuated tube. In the second, a molecular beam of selenium was impinged on the surface in a continually pumped ultrahigh vacuum system.

The apparatus used for the free vapor experiment is shown in Figure 2. It consisted of a Pyrex glass vessel containing "reagent" grade selenium triply distilled *in vacuo*. The vessel was sealed off at a gauge pressure of 10^{-8} mm Hg. The pressure inside, however, may have been significantly greater, since glass shows considerable outgassing upon melting. The vessel was placed in a three zone electrical furnace in which each zone could be separately controlled, and six thermocouples were mounted in the numbered positions shown in the figure. At one end of the vessel was a re-entrant tip into which a Pyrex glass probe could carry a cooling gas; a thermocouple wire was inserted alongside the probe with its junction in the bulb at the end of the tip. The tip itself was located opposite a Pyrex glass sight port in the furnace. Nucleation on the tip could be observed visually at 15x through a stereomicroscope.

In operation, zone 1, zone 2, and the tip were initially held at a temperature about 10°C above zone 3, which contained the selenium and therefore determined the vapor pressure in the vessel. This also prevented condensation of selenium in other zones;

specifically, "fogging" of the glass beneath the sight port. A flow of N_2 gas was then used to lower the re-entrant tip temperature below the temperature of zone 3 until nucleation occurred. Approximately 10 minute periods were allowed between 1°C decreases in temperature near the nucleation temperature, T_{nuc}. This temperature defined P_e for the free vapor case.

The tip temperature was then raised by the same procedure until evaporation was observed, in order to determine T_{evap}, which defined P. This temperature corresponded to the temperature of zone 3. Both measurements, however, were taken with the tip thermocouple. The entire procedure was repeated for six zone 3 temperatures, T_{evap} between 145°C and 320°C.

The molecular beam work was also performed in a Pyrex glass apparatus containing vacuum distilled selenium; this system, however, was pumped to operating pressures of 10^{-9} to 10^{-10} mm Hg (as measured in the tip chamber), using standard ultrahigh vacuum techniques, including repeated system bakeouts at 450°C. The vessel itself contained an integral, liquid nitrogen dewar (to insure efficient condensation of scattered selenium), and a re-entrant tip into which a nichrome wire heater and thermocouple were inserted, as shown in Figure 3. The source chamber was placed in an electrical furnace of identical construction to a single zone of the free vapor furnace, and the orifice heated independently

with heater tape. The whole oven assembly protruded through a hole below the vacuum table, which allowed the source chamber to be cooled while selenium was being transferred from tip to source chamber at the end of a run.

The technique used in the molecular beam experiment was the following: The source chamber was first heated to the desired temperature, and the orifice to a temperature 50°C higher. Concurrently, the tip was heated to 350°C to keep it as free of contamination as possible. The integral liquid nitrogen dewar was then filled to effect collimation. This produced a molecular beam of constant intensity impinging through the two circular collimating slits onto the re-entrant tip. The temperature of the tip was reduced slowly until nucleation was observed; again this temperature defined P_e. The temperature was then increased slowly to obtain T_{evap}, which in this case did not equal the source temperature. As before, T_{evap} defined P. To repeat the procedure, it was necessary to close a ground glass slider valve which sealed the selenium part of the vacuum system from the upper trap and pumping system. The high vacuum side of the system was then baked at 450°C, which transferred the selenium into the source chamber below the table: six such runs were performed, ranging from 120°C to 160°C in T_{evap}.

RESULTS

The quantitative results obtained are shown in Figure 4, a plot of $\ln \alpha_{crit}$ versus $1/T_{nuc}$. Earlier results shown for comparison were obtained by Hudson[1,2] for zinc and cadmium nucleated on Pyrex glass using the free vapor technique. The theoretically expected temperature dependence of α_{crit} is indicated by the dotted line for the case of the selenium free vapor experiment. This line was normalized to the data at the highest temperature point taken. Direct calculation of the value of $\ln \alpha_{crit}$ expected from nucleation theory without normalization gives values greater than those observed by a factor of 10^3-10^4. The normalized theoretical curves for the other data would show similar departures.

As far as nucleus morphology is concerned, the phase nucleated in the free vapor case was the liquid, even though the nucleation temperatures observed cover a range extending to 90°C below the equilibrium melting point. In the molecular beam case, the phase nucleated was invariably red solid, the equilibrium phase in the temperature range of experiment. Note, too, that even in the region in which the observed nucleation temperatures and supersaturations overlap for the two techniques, this difference in the phase nucleated persists.

It was also observed in the molecular beam case that the measured nucleation and evaporation temperatures were dependent

upon the processing the system had received. This dependence can be summarized by stating that as the system received repeated bakeouts, the observed values of T_{nuc} and T_{evap} for a given effusion cell (source) temperature rose monotonically to reach a limiting value after many bakeouts, but that the difference between these temperatures in any given run, and consequently the value of α_{crit} calculated from them, changed only slightly. This behavior is shown in Table 1.

DISCUSSION

The most striking result of the measurements made is the observed difference in the phase nucleated under nominally identical conditions of temperature and supersaturation for the free vapor and molecular beam experiments. The only physical differences in the two experiments were the vapor temperature for a given impingement rate (much higher in the molecular beam case), and the level of surface contamination in the system (higher in the free vapor case).

The vapor temperature could affect the process of nucleation only through imperfect thermal accommodation. That is, if energy transfer between beam and substrate were less than complete, the adsorbed species would have a shorter lifetime on the surface, and the equilibrium adatom population would be correspondingly reduced. Such a process would increase the

apparent supersaturation required to cause appreciable nucleation, but it is hard to conceive of a mechanism whereby a reduced adatom population could lead to a change in nucleus morphology. Moreover, the observed critical supersaturations in the molecular beam case were smaller than the free vapor case. This is not unequivocal evidence of the lack of a thermal accomodation effect, as the phase nucleated was not the same in both cases, but it does indicate that such effects, if present do not differ greatly from one case to the other.

Thus it appears that the difference in surface contamination is the factor responsible for the change in nucleus morphology. This is a reasonable choice on several grounds. In any system, the nucleus which will form at the lowest supersaturation is the one of lowest ΔG_i^*. This ΔG_i^* is determined by the balance of the decrease in bulk free energy obtained in forming the nucleus and the increase in surface free energy involved in the new interfaces formed. The bulk free energy changes are not greatly different[6] for the various condensed phases of selenium, as evidenced by the ease with which bulk liquid selenium may be supercooled drastically without crystallizing. On the other hand, the difference in the interfacial energy terms may be

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6. Herre, R., Naturwissenschaften, vol. 44, no. 2, p. 31, Jan. 20, (1957)

[illegible] one [illegible]

[illegible]

residual gas.

One can make the intuitive argument that [illegible] would increase the critical [illegible] through [illegible] the substrate-vapor interfacial energy and increasing the substrate-nucleus free energy, both of which would [illegible] increase $\phi(\theta)$ and thus σ_{crit}. This argument has been [illegible] advanced by Hirth and Pound[4]. If such an effect is [illegible] for the change in nucleus morphology, one must also [illegible] that the substrate-nucleus interfacial energy [illegible] rapidly with adsorbed coverage for the crystalline [illegible] it does for the liquid nucleus. In other words, [illegible] on a clean surface, the diff[illegible] are small enough that the [illegible] crystalline phase is the [illegible] process, while for nucleation [illegible] surface, the [illegible] surface energy terms [illegible] override the difference in bulk [illegible] energies.

One can make the alternative argument that the [illegible] in behavior arises from kinetic considerations. The [illegible]

form of selenium at the temperatures of the present work is Se_8,[7] which exists as an eight-membered ring. It is possible that on the clean surface some "templating" action occurs either through orientation in the adlayer or through orientation of suberitical clusters at microscopic crystalline patches on the substrate. This "templating" would aid in the formation of a crystalline nucleus. On the dirty surface, however, one would expect such orienting influences to be somewhat masked by the adsorbate, resulting in the formation of a liquid nucleus. The present techniques were not sufficiently detailed to permit a choice between these two alternative explanations.

In contrast to this behavior, the quantitative form of the $\ln\alpha_{crit}$ versus $1/T_{nuc}$ relation observed does not appear to be greatly influenced by adsorption. The general form of this relation is the same for both free vapor and molecular beam cases, and moreover is quite similar to that previously observed for zinc and cadmium on similar Pyrex substrates. In addition, this general form appears to be independent of the vapor temperature

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7. a) Hodgman, Charles, Ed., Handbook of Chemistry and Physics, 44th Edn., Chemical Rubber Publishing Co., Cleveland, P. 644, (1963)

   b) International Critical Tables.

for a given flux, indicating that thermal accommodation effects are either absent or have a constant effect on the nucleation rate in the system studied. Thus the observed $\ln \alpha_{crit}$ versus $1/T_{nuc}$ relation does appear to be representative of the inherent kinetic steps in the nucleation process. Attempts have been made to fit the data of this work to the theoretical predictions of both cap-nucleus and disc-nucleus models, but without success. The data definitely do not fit either relation, but the reasons for this lack of agreement are not obvious.

Finally, we may consider the observed variation of the nucleation and evaporation temperatures at a given impinging flux with repeated bakeouts. The observed increase in these temperatures indicates that for a constant actual flux to the surface, the effective flux increased with repeated bakeouts (and consequently smaller amounts of substrate surface contamination) until a steady state value was reached, which was unaltered by further bakeout. This indicates that an accommodation barrier exists to the adsorption of selenium on gas-covered Pyrex, which disappears when the surface is cleaned. This is definitely an adsorbed impurity effect, rather than a change in surface structure, since it reappeared after the system had been exposed to water vapor and carbon dioxide, and could again be removed by further bakeout. The detailed mechanism of this effect is not obvious,

although adsorption of residual gases, which would generally lower the surface energy of the substrate might reduce the stay time of an adsorbed Se_8 molecule to a value shorter than the time required for its reorientation to a stable adsorbed position.

CONCLUSION

It has been shown that impurity adsorption can play a dominant role in both the morphology of the nucleus formed in condensation on substrates and in the detailed kinetics of the adsorption process. However, this impurity adsorption does not appear to greatly effect the form of the $\ln\alpha_{crit}$ versus $1/T_{nuc}$ relation.

It would be highly desirable to pinpoint the impurity species responsible for these effects, and to demonstrate its action unequivocally by observing the change in nucleus morphology on the addition of known and controlled amounts of this active impurity. Such a procedure was not possible in the present work, as the system used was not equipped for either residual gas analysis or controlled gas introduction. Further work along these lines is presently in progress.

ACKNOWLEDGMENT

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TABLE 1

Effect of Number of Bakeouts on Nucleation Parameters in Molecular Beam Experiment

No. Bakeouts	T_{evap}(°C)	T_{nuc}(°C)	ΔT	P_{min}	T_{80}(°C)
8	143	133	10	$7(10^{-10})$	275
12	145 max.	138 max.	7	$3(10^{-10})$	
9	147	141	6	$6(10^{-10})$	300
13	157 max.	150.5 max.	6.5	$7(10^{-10})$	
9	150	144	6	$7(10^{-10})$	325
14	160.5 max.	155 max.	5.5	$5(10^{-10})$	

LIST OF CAPTIONS

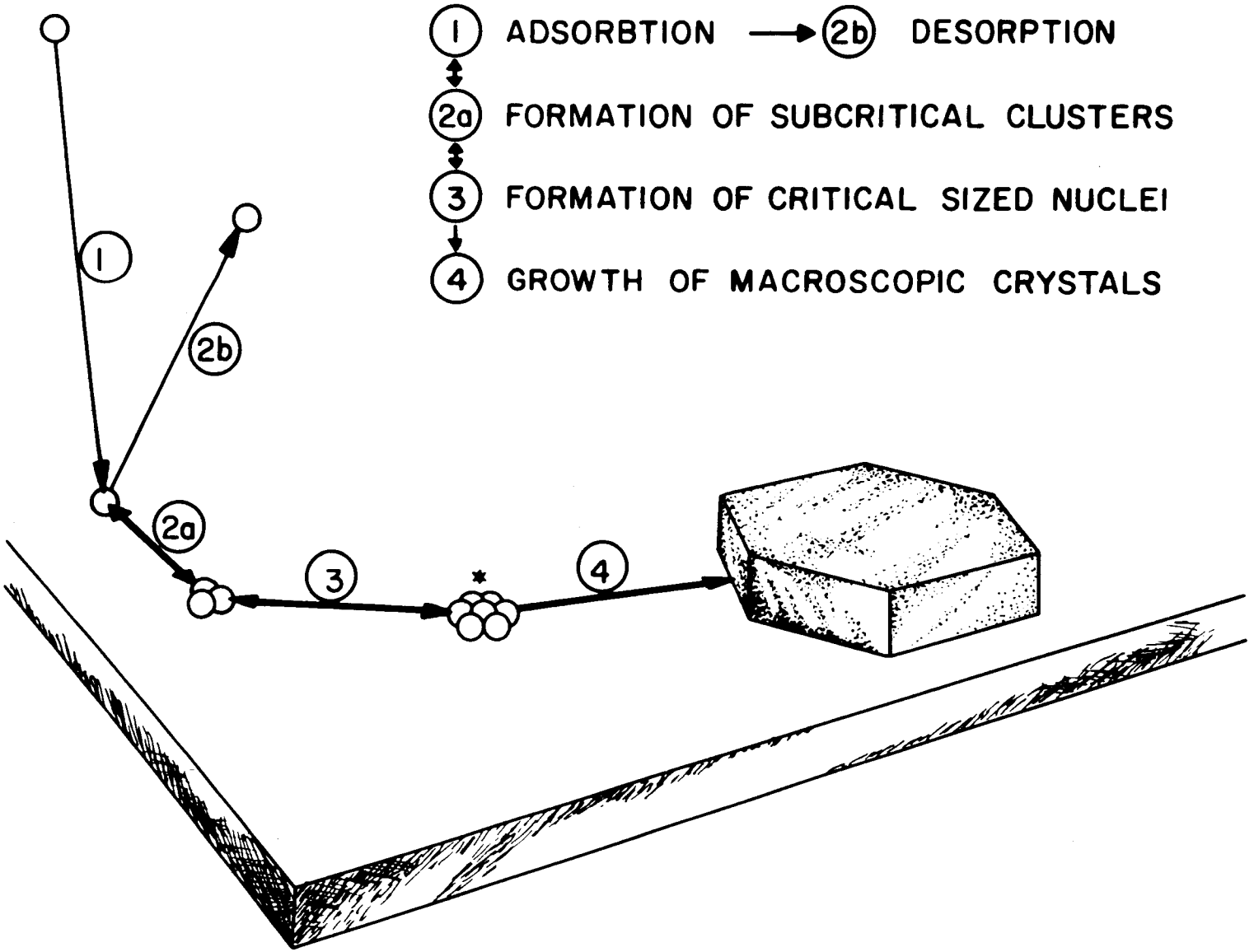
Figure 1: Steps in Heterogeneous Nucleation of Crystal or Liquid from Vapor

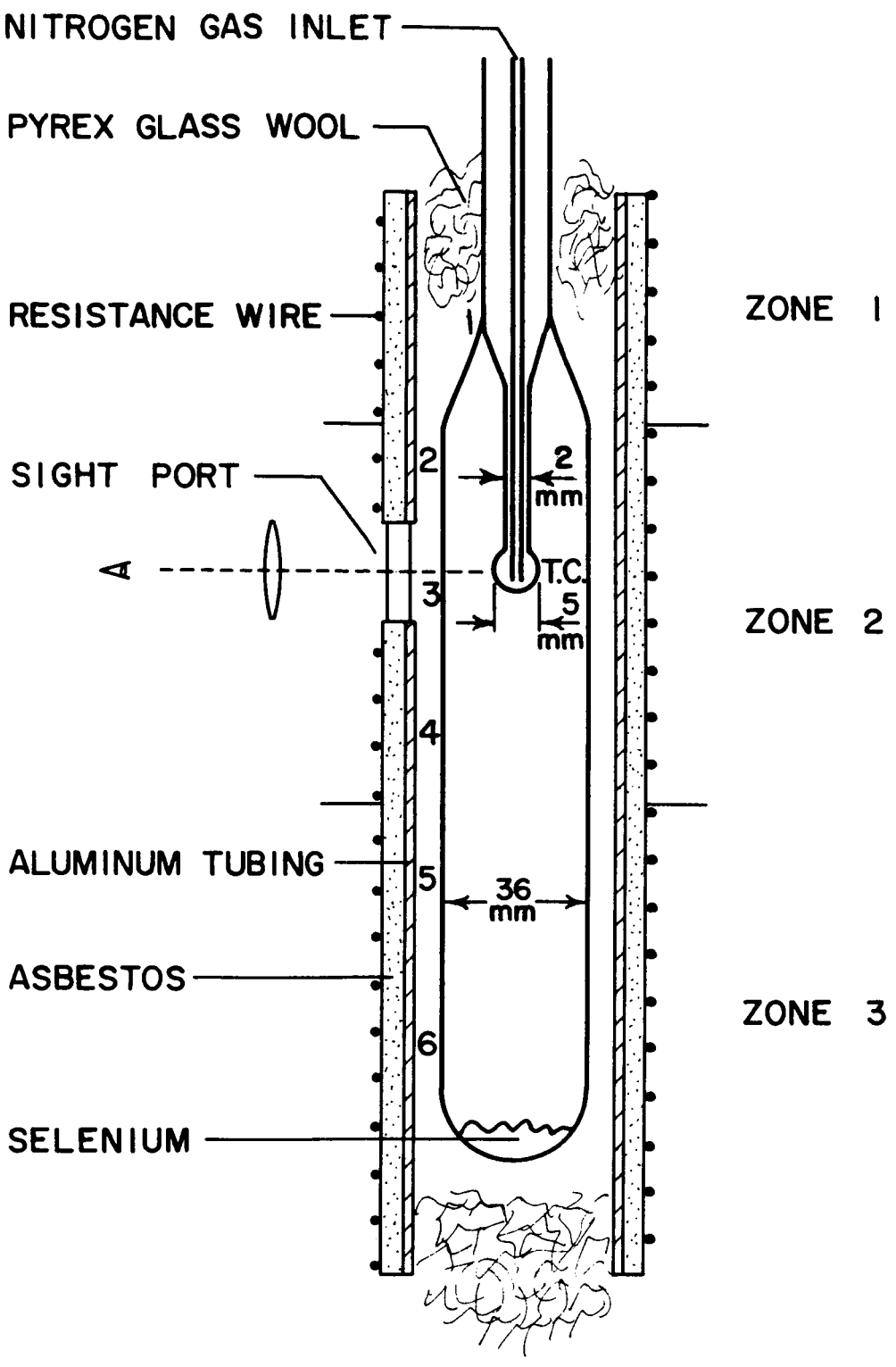
Figure 2: Selenium Free-Vapor Apparatus

Figure 3: Selenium Molecular Beam Apparatus

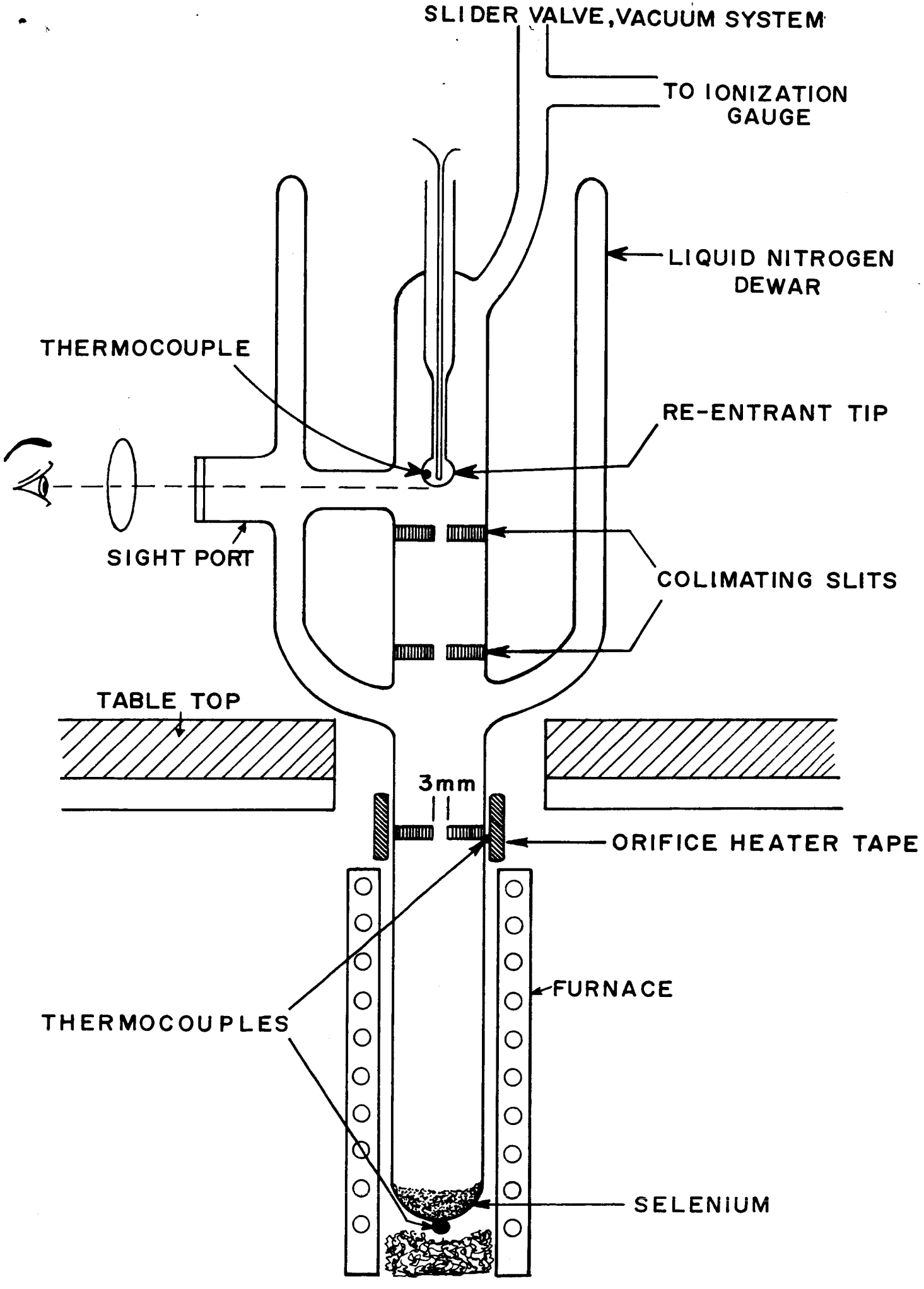
Figure 4: Plot of $\ln a_{crit}$ versus $1/T_{nuc}$

STEPS IN HETEROGENOUS NUCLEATION OF CRYSTAL FROM VAPOR





SELENIUM FREE-VAPOR TUBE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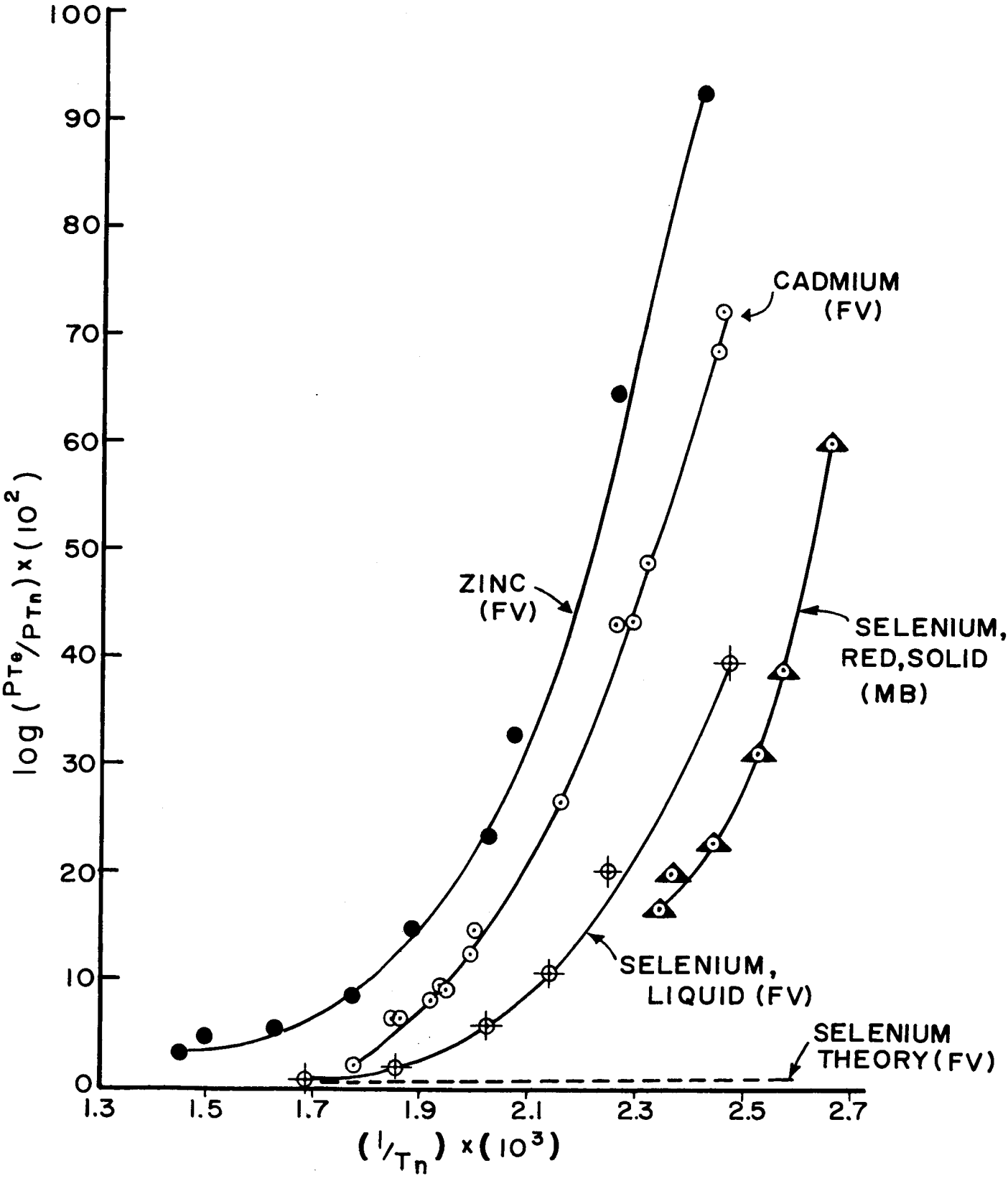
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(1/Tn) x (10³)
CADMIUM (FV)
ZINC (FV)
SELENIUM, RED, SOLID (MB)
SELENIUM, LIQUID (FV)
SELENIUM THEORY (FV)